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[2,3:5,6]DICYCLOBUTAPYRIDINE

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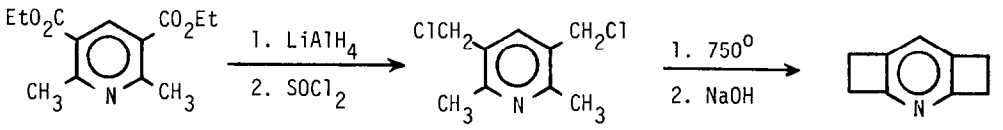
The pyrolytic elimination of hydrogen chloride from α-chloro-o-xylene and related compounds has recently permitted the facile preparation of a variety of cyclobutene-fused benzene[1] and naphthalene[2] systems as well as 6-radialene[3]. In this paper we would like to present the extension of this technique to pyridine derivatives with the preparation of [2,3:5,6]dicyclobutapyridine (3).



1 2 3

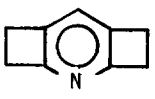
Lithium aluminum hydride reduction of 3,5-dicarbethoxy-2,6-dimethylpyridine (1)[4] provides the corresponding diol. Treatment of this diol with thionyl chloride then affords 2,6 -dimethyl-3,5-di(chloromethyl)pyridine (2), mp 107-108°C.[5] The pyrolysis reaction is carried out by subliming 0.4 g (2.0 mmol) of dichloride 2 into a quartz pyrolysis tube (25mm o.d. x 33 cm long and filled with pieces of quartz glass tubing) which had been previously evacuated to 0.1 mm and heated to 750°C. The crude pyrolysate was collected on a cold finger filled with liquid nitrogen and then washed from the cold finger with 20 ml of water. The aqueous solution was made basic with sodium hydroxide and extracted thoroughly with ether. After drying over $MgSO_4$, the ether was evaporated to give 160 mg of a brown oil which was analyzed by vpc. The crude material showed a single major peak at 2.8 min retention time on a column of 10% Carbowax 20M + 5% KOH on Chromsorb W (10 ft x 1/8 in at 130°C and 30 cc/min). Preparative vpc provided 38 mg (15%) of pure crystalline 3, mp 117-118°C.

Compound 3 exhibited the following spectral properties: ^{1}H NMR ($CDCl_3$, 100 MHz) δ7.00 (s, 1H, C_4-H), 3.32 (m, 4H, α-CH_2), and 3.00 ppm (m, 4H, β-CH_2); ^{13}C NMR ($CDCl_3$, 25.15 MHz) δ161.7 (C_2), 138.6 (C_3), 124.6 (C_4), 34.2 (α-CH_2), and 26.8 ppm (β-CH_2); a proton-coupled ^{13}C nmr revealed the following coupling constants: J_{C4-H} = 163.2 Hz (d), $J_{C\alpha-H}$ = 138.9 Hz (t), and $J_{C\beta-H}$ = 139.8 Hz (t) (some long range coupling was also apparent); UV (95% ethanol) λ_{max} 290 nm (ε8078); IR (KBr) 2970, 2930, 1594, 1546, 1423, 1365, 1250, 1210, 1140, 1095, amd 904 cm^{-1}; Anal. Calcd for C_9H_9N: m/e 131.0735. Found: m/e 131.0741.

The relatively large aromatic C-H coupling constant (compare with a value of 152.2 for 1,2,3,4,5,6,7,8-octahydroacridine) can be explained by invoking significant rehybridization of the bridgehead carbon atoms.[6,7] The aromatic proton chemical shift is seen to occur at higher field than the next known homolog ([2,3:5,6]dicyclopentapyridine δAr-H = 7.30 ppm). Similar behavior has been noted for the corresponding para-bis-annelated benzenes.[8] The UV absorption continues a previously established trend, shifting to longer wavelength and higher intensity.[6]

The basicity of dicyclobutapyridine 3 was determined as a half-neutralization potential by titration at 25°C with 0.10 N perchloric acid in acetic acid with acetic anhydride as the solvent.[9] The resulting pK_a is shown in Table I along with the values for other relevant compounds. It is interesting to note the very regular change in basicity with decreasing ring size along the para-bis-annelated series. A drop of about one pK_a unit occurs with the loss of each methylene unit. The influence of four-membered ring fusion is also seen to be additive with respect to pyridine: one four membered ring causes a drop of 0.45 pK_a units while two cause a drop of 0.90 units. The normal alkyl inductive effect causes increased basicity so that these decreases must again be explained by rehybridization theory.

Table I. Basicities of Some Annelated Pyridines (pK_a)[6,7]



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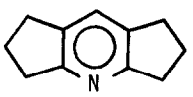

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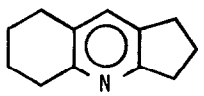

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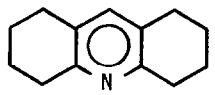

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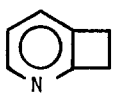

4.85

5.30

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